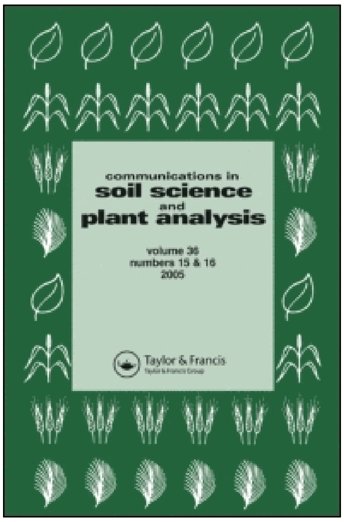

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Atrazine and Metolachlor Sorption to Switchgrass Residues

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Atrazine and Metolachlor Sorption to Switchgrass Residues

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Abstract: Herbicide retention by residue mulch in vegetative filter strips could be an effective attenuation mechanism for removing herbicides from runoff. Adsorption studies were conducted to quantify the amount of atrazine and metolachlor that can be adsorbed and removed from runoff by thatch or fresh switchgrass residue. Adsorption of C^{14}-atrazine and metolachlor on thatch or fresh switchgrass residue was conducted by using concentrations of 2.5, 7.5, 13.2, and 26.4 $\mu mol\,L^{-1}$ and a 24-h equilibration period. Adsorption coefficients (K_d) decreased in the order, atrazine sorption on fresh switchgrass residue (81.1 $L^{-1}\,kg^{-1}$), metolachlor sorption on fresh residue (32.9 $L^{-1}\,kg^{-1}$), atrazine sorption on thatch residue (21.4 $L^{-1}\,kg^{-1}$), and metolachlor sorption on thatch switchgrass residue (15.1 $L^{-1}\,kg^{-1}$). On a volumetric basis ($K_{d\text{-}vol}$), only atrazine showed a significantly greater $K_{d\text{-}vol}$ value on fresh residue than on the thatch residue. Absorption through cut ends of the residues (especially the fresh residue) may have produced adsorption capacities that would not be observed under field conditions. Fresh or thatch switchgrass residue in vegetative filter strips can help abate atrazine and metolachlor by intercepting and sorbing some of the herbicides.

Keywords: Switchgrass, atrazine, metolachlor, vegetative filter strip

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INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-1-methylethyl) acetamid] are two widely used herbicides that control annual broadleaf and grass weeds in a variety of crops. Atrazine is primarily used in corn (*Zea mays* L.) and sorghum [*Sorghum bicolor* (L.) Moench], whereas metolachlor is used in corn, soybean (*Glycine max* L. Merr.), and potato (*Solanum tuberosum* L.). Both atrazine and metolachlor can move out of treated agricultural fields via runoff to various water bodies. For field-applied atrazine, it is estimated that about 2–5% can be lost to surface water systems (Wauchope 1978). Transport of atrazine and metolachlor with runoff has led to their detection in numerous surface water systems throughout the United States (Goolsby et al. 1994; Spalding et al. 1994; Clarke and Goolsby 2000).

Best management practices are recommended to reduce atrazine and metolachlor transport to surface water. One such practice is the use of vegetative filter strips, which are strips of closely grown vegetation, usually grasses, positioned downslope at the edge of fields. They are used to filter nutrients, sediments, organics, pathogens, and pesticides from agricultural runoff before they reach water systems. Switchgrass (*Panicum virgatum* L.), a warm-season perennial, is widely adapted in North America and is well suited for use in filter strips because it has an erect and stiff stem. Dabney et al. (1995) reported that switchgrass is not easily covered with sediment and, therefore, maintains its effectiveness as a filter strip grass for a long period of time. Switchgrass filter strips have been shown to be effective in removing sediment, nutrients, and herbicides including atrazine and metolachlor from runoff (Sanderson et al. 2001; Mersie et al. 1999). Infiltration of runoff into the filter strip has been shown to be a major mechanism for removal of dissolved pesticides from runoff (Mersie et al. 1999). The role that the switchgrass vegetation has in removing herbicides from runoff has not been fully explored.

Herbicide retention by residue mulch at the soil surface has been reported in conservation production systems. Studies in no-till systems have shown that straw or decaying organic matter on the soil at the time of herbicide application reduces soil reception of many herbicides (Banks and Robinson 1984). Hall et al. (1984) reported that stover mulched surfaces in no-till corn significantly reduced runoff and retained a majority of the applied cyanazine {2-[(4-chloro-6-(ethylamino)-s-triazin-2-yl)amino]-2-methylpropionitrile}. Banks and Robinson (1986) reported in a field study, that wheat straw at 4480 kg ha^{-1} retained 16.7% of the applied metolachlor. The sorption of the herbicide, chlorimuron ethyl, was greater in rye and hairy vetch residues than in soil from no cover crop or soil beneath the residue (Reddy et al. 1995). In a laboratory experiment, zoysiagrass (*Zoysia japonica* Steud.) thatch significantly reduced the leaching of dicamba in columns (Rautri et al. 1997). The surface layer of zoysiagrass thatch also had a much higher sorptive capacity than the underlying soil. Presently, there is no published information on the type and quantity of herbicides that can be retained from runoff by switchgrass residue. The objective of this study is to determine the atrazine and metolachlor adsorption capacities of fresh and thatch switchgrass residues.

MATERIALS AND METHODS

Thatch and fresh residue samples were collected from an 8-year-old stand of switchgrass at Virginia State University's experimental farm. The switchgrass was established and maintained without the use of herbicides and contained a 5- to 10-cm-thick thatch layer. Three-square meter plots were randomly selected from which the thatch and fresh residue samples were collected. The thatch was collected during July, which consisted of nondecomposed and partially decomposed switchgrass residue. A hand rake was used to collect the thatch and then stored and air dried in a shed until used. Care was taken to avoid collecting soil with the thatch. Freshly cut switchgrass was collected from the same square meter plots by using hand clippers and used within 12-h. Herbicide adsorption analyses were conducted on residue (fresh and thatch) from each plot.

The sorptive capacity of the thatch and fresh switchgrass residue was determined by using a modified batch/flow technique that minimized the disruption of organic residues (Rautri et al. 1997). The experiment was conducted by using 60-mL glass syringe barrels. Thatch or fresh switchgrass samples, having an oven dry weight of 6 g, were cut into 2-cm length and loaded to 25-mL in a glass syringe barrel for the thatch grass and to 50-mL for the fresh grass. Before packing the residue, a 3.7-cm glass fiber filter was placed at the bottom of the glass syringe barrel. After packing, a 3.2-cm diameter $\times$ 1.5-cm foam plug was placed above the grass and a second 3.7-cm-diameter glass fiber filter was placed on top the foam plug. A vacuum flask was placed under the syringe barrel to collect the leachate after it passed through the switchgrass residue column.

Herbicide solutions (in 0.01 M $CaCl_2$) were prepared by mixing ^{14}C-ring labeled and technical grade chemical to obtain concentrations of 2.5, 7.5, 13.2, and 26.4 $\mu mol\,L^{-1}$ of atrazine or metolachlor. Technical grade and ^{14}C-labeled metolachlor and atrazine were obtained from Syngenta (Greensboro, NC). Specific activity was 102 $MBq\,mmol^{-1}$ for atrazine and 202 $MBq\,mmol^{-1}$ for metolachlor. Radiopurity was 98.5% for atrazine and 98.9% for metolachlor. Purity of technical grade atrazine and metolachlor were 98% and 97%, respectively.

A 30-mL aliquot of herbicide solution was placed in a burette located directly above the syringe barrel. The herbicide solution was then leached through samples of thatch or fresh switchgrass residue over a 24-h period by using a calibrated vacuum extractor. The leachate was collected in a vacuum flask placed under the syringe barrel. After the 24-h leaching period, vacuum was applied to drain any remaining herbicide solution from the grass in the syringe into the collection vacuum flask. Amounts of ^{14}C-labeled chemicals in the leachate were determined by pipetting 1-mL of the leachate into 10-mL of scintillation fluid (Scintverse E, Fisher Scientific, Pittsburgh, PA) and counting it by a liquid scintillation spectrometer (LSS) using LKB 1219 RackBeta scintillation counter (Wallac Oy, Turku, Finland). Atrazine and metolachlor sorbed to any material other than the thatch or fresh switchgrass residue were taken into account by washing the glassware and the foam plug as well as the amount retained on the glass filters. The burette, the glass syringe, and the foam plug each were washed with 10-mL of 5% methanol aqueous solution (v/v). A 1-mL sample was taken from each wash solution, and the ^{14}C was counted as described above. The two glass fiber filters were placed directly into the scintillation fluid for ^{14}C measurement by LSS. Amounts of chemicals sorbed on switchgrass residue were determined by difference in the initial amount (solution in the burette) and leachate (solution in the collecting vacuum flask) and were adjusted to include technical grade material. The initial amounts were corrected for herbicide detected in the wash solutions of the burette, syringe, and foam plug as well as any amount retained on the glass filters.

The treatments were conducted in triplicate in a completely randomized design. Data were subjected to general linear models in SYSTAT Software (2002). Treatment means were separated by using standard errors. Other statistical evaluations included calculation of 95% confidence intervals on K_d and K_f values, as well as performing regression analysis on adsorption isotherms. Statistical differences were determined at the 0.05 probability level.

RESULTS AND DISCUSSION

The linear adsorption isotherms for atrazine and metolachlor show good fit to the measured data, $r^2 = 0.99$ (Figure 1). Both the adsorption distribution coefficient (K_d) and Freundlich adsorption coefficient (K_f) were calculated (Table 1). The K_d value is defined as $(x/m)/C$, where x is the amount of chemical adsorbed, m is the amount of adsorbent, and C is the chemical concentration at equilibrium. In the Freundlich equation, $1/n$ takes into account the nonlinearity in the adsorption isotherm. When $n = 1$, adsorption is linearly proportional to the equilibrium solution concentration, thus, a distribution coefficient (K_d) can be used to adequately describe adsorption. The $1/n$ values for atrazine or metolachlor adsorption on fresh switchgrass residue were not significantly different from unity (Table 1). However, the $1/n$ values for adsorption on thatch residue were significantly different from unity. This finding indicates that the Freundlich adsorption isotherm is more appropriate to use for adsorption on thatch residue. However, there was no significant difference between the K_f and K_d values. Therefore, the K_d values are

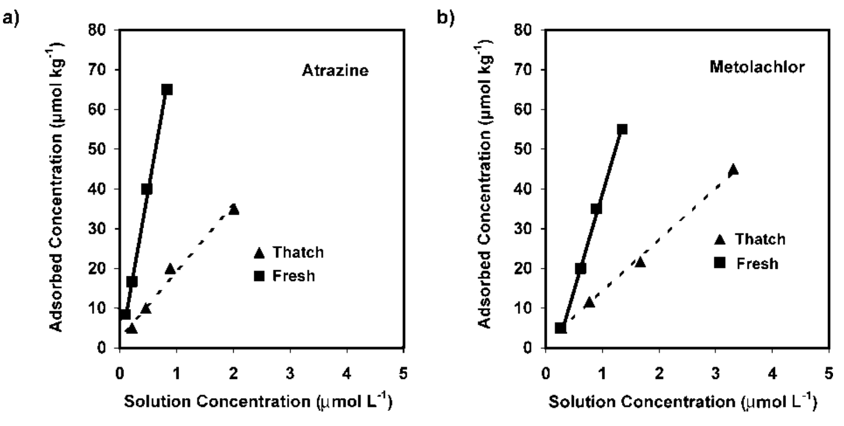

Figure 1. (a) Atrazine and (b) metolachlor adsorption isopleths at four herbicide concentrations (2.5, 7.5, 13.2, and 26.4 μmol L^{-1}) on switchgrass thatch and fresh residue.

used for comparison of herbicide adsorption capacities between the two residue types.

The K_d values for both atrazine and metolachlor adsorption on switchgrass residue are larger than those reported for mineral soils (Seybold et al. 1994; Seybold and Mersie 1996). Other studies have shown greater pesticide adsorption capacities on thatch or dry straw than on soil for fungicides (Dell et al. 1994) and herbicides (Reddy et al. 1995; Rautri et al. 1997). High organic matter soils have much higher atrazine and metolachlor K_d values (i.e., 40 and 66 L kg^{-1}, respectively) than low organic matter mineral soils (Mersie and Seybold 1996; Seybold and Mersie 1996). The atrazine and metolachlor K_d values for the switchgrass residue are similar to the K_d values obtained for high organic matter soils (>9% organic C).

Adsorption of atrazine was significantly greater than that for metolachlor on both thatch and fresh residues (Table 1). This finding suggests that switchgrass would be more effective at removing atrazine than metolachlor from runoff in VFS. Because there was a twofold difference in bulk density between the two residue types, adsorption capacity of the residue was placed on a volumetric basis ($K_{d\text{-}vol}$) (Table 1). On a volumetric basis, sorption of atrazine was significantly greater on fresh residues than sorption on thatch residues. There was no significant difference in metolachlor sorption ($K_{d\text{-}vol}$) between the two residues. In general, atrazine sorption ($K_{d\text{-}vol}$) on both residues was significantly greater than that for metolachlor.

The switchgrass residues were cut into segments, exposing numerous cut ends in the adsorption study. It is possible that greater amounts of atrazine or metolachlor could have absorbed into the nearly "live" fresh tissue than that of the dry residue during the 24-h leaching process. This may explain the greater adsorption capacity of the fresh residue. Under field conditions, cut ends would not be exposed to runoff, unless the VFS was mowed or cut. The

Table 1. Atrazine and metolachlor Freundlich adsorption coefficients (K_f) and slopes ($1/n$) and adsorption distribution coefficients (K_d) for thatch and fresh switchgrass residues ($K_{d\text{-}vol}$ is the K_d on a volumetric basis)

Herbicide	Grass	K_f ($\mu mol^{1-1/n} L^{1/n} kg^{-1}$)	$1/n$	r^2	K_d ($L\,kg^{-1}$)	$K_{d\text{-}vol}$ ($L\,M^{-3}$)
Atrazine	Thatch	20.1 (16.4–24.6)[a]	0.88 (0.05)[b]	0.99	21.4 (18.7–24.1)[a]	5.1 (4.5–5.8)[a]
	Fresh	79.4 (69.5–89.1)	0.98 (0.02)	0.99	81.1 (71.9–90.3)	9.7 (8.6–10.8)
Metolachlor	Thatch	15.0 (12.7–17.7)	0.86 (0.04)	0.99	15.1 (12.7–17.5)	3.6 (3.0–4.2)
	Fresh	38.5 (29.8–49.0)	0.96 (0.08)	0.99	32.9 (23.4–42.4)	3.9 (2.8–5.1)

[a]Numbers in parentheses are 95% confidence intervals (CI). For K_f, the CIs are the antilogs of $\log K_f - \mathrm{CI} \log K_f$ and $\log K_f + \mathrm{CI} \log K_f$.

[b]Numbers in parentheses are standard errors.

sorption capacities under laboratory conditions using cut residue segments may not represent true sorption capacities of switchgrass that would occur in VFS.

Switchgrass has a life cycle of 10 or more years. During this time, switchgrass residue from senescent leaves and shoots will accumulate in the filter strip. This thatch layer from aboveground vegetation can intercept and adsorb pesticides as runoff moves through the filter strip. The organic residue can also absorb and retain water that would otherwise be lost in runoff. The degree of degradation or age of the residue may affect how effective it is in adsorbing herbicides from runoff. Live or recently fallen fresh switchgrass residue can intercept and retain herbicides from runoff, especially if there are many exposed cut ends. When designed to allow for runoff (through sheet flow) to come into contact with the thatch, adsorption to switchgrass could be a significant attenuation mechanism for removing dissolved pesticides from runoff passing through a VFS.

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